

First-principles approach to lattice-mediated magnetoelectric effects

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We present a first-principles scheme for the computation of the magnetoelectric response of magnetic insulators. The method focuses on the *lattice-mediated* part of the magnetic response to an electric field, which we argue can be expected to be the dominant contribution in materials displaying a strong magnetoelectric coupling. We apply our method to Cr_2O_3 , a relatively simple and experimentally well studied magnetoelectric compound.

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Magnetoelectric (ME) materials are insulators that allow control of their magnetic properties by means of external electric fields [1, 2], thus attracting great technological interest. Current research focuses on obtaining compounds with a robust ME behavior at ambient conditions. This is proving a major challenge, as progress is hampered by one fundamental difficulty: the scarcity of ferromagnetic insulators (not to mention ferromagnetic and ferroelectric multiferroics [3]) with a high Curie temperature. An additional problem pertains to the magnitude of the effect: the ME response is usually very small, reflecting the weakness of the spin-orbit interactions that are typically responsible for the coupling.

Quantum calculations based on efficient schemes like Density Functional Theory (DFT) have proved very useful in studies of magnetic and ferroelectric materials, and are expected to facilitate progress on magnetoelectrics. Indeed, there is a growing number of DFT works tackling the search for new compounds [4] and even proposing new coupling mechanisms [5, 6]. However, we still lack a first-principles scheme to compute the ME coupling coefficients, something that is critical to aid the experimental work. In this Letter we introduce one such *ab initio* methodology and demonstrate its utility with an application to Cr_2O_3 .

Lattice-mediated ME response.— Computing the full ME response of a material would require quantum relativistic simulations with simultaneously applied electric and magnetic fields. While possible in principle, such calculations constitute a great challenge even for the case of static fields, and it is convenient to look for simplifications of the problem.

In the following arguments we will consider an idealized one-dimensional (1D) crystal displaying a linear ME effect, the generalization being straightforward. At zero magnetic field, the magnetization induced by the application of an electric field \mathcal{E} is given by:

$$\Delta\mathcal{M}(\mathcal{E}) = \mathcal{M}(\mathcal{E}) - \mathcal{M}^S = \alpha\mathcal{E} + \mathcal{O}(\mathcal{E}^2), \quad (1)$$

where α is the linear ME coefficient and we have included a spontaneous magnetization \mathcal{M}^S for generality. The magnitude of the ME response is limited by the magnetic (χ^m) and dielectric (χ^d) susceptibilities as

$\alpha^2 < \chi^d\chi^m$ [7], which suggests that strong ME couplings will occur in materials displaying large dielectric and magnetic responses. On more physical grounds, one can argue that large ME effects will be associated to significant electronic hybridizations or orbital rearrangements induced by applied electric fields, as it is processes of that nature that may lead to a magnetic response via the spin-orbit coupling. It is then worth noting that (1) such a response to an electric field is typical of essentially all highly polarizable compounds used in applications and, most importantly, (2) such strong dielectric responses are never a purely electronic effect; rather, they are driven by the *structural* changes induced by the applied field. One can thus conclude that large ME effects will most likely be based on *lattice-mediated* mechanisms.

Formally, the lattice-mediated contribution to the dielectric susceptibility is defined as $\chi_{\text{latt}}^d = \chi^d - \chi_{\text{elec}}^d$, where χ_{elec}^d accounts for the purely electronic effect corresponding to clamped atomic positions and lattice parameters. The ME coupling coefficient α can also be decomposed in this way, and the discussion above suggests that α_{latt} will be the leading contribution in materials displaying strong ME effects. We shall thus focus on its computation.

Methodology.— The structural response of an insulator to a *small* electric field can be modeled in terms of the infra-red (IR) modes of the material, which are obtained from the diagonalization of the force-constant matrix at the Γ point of the Brillouin zone (BZ). (Working with small fields allows us to truncate all the following Taylor series at the lowest order possible.) Let us denote by u_i the amplitude of the i -th IR mode, with i running from 1 to N_{IR} , and by C_i the corresponding eigenvalue. Taking the u_i 's and the applied field \mathcal{E} as independent variables, we write the energy of our idealized 1D crystal around its equilibrium state as

$$E(\{u_i\}, \mathcal{E}) = E_0 + \frac{1}{2} \sum_{i=1}^{N_{\text{IR}}} C_i u_i^2 - \Omega_0 \mathcal{E} [\mathcal{P}^S + \chi_{\text{elec}}^d \mathcal{E} + \Delta\mathcal{P}_{\text{latt}}(\{u_i\})], \quad (2)$$

where Ω_0 is the unit cell volume and we have included a spontaneous polarization \mathcal{P}^S for generality. Note we

have decomposed the linear part of the induced polarization into electronic ($\chi_{\text{elec}}^{\text{d}} \mathcal{E}$) and lattice contributions, the latter being given by

$$\Delta \mathcal{P}_{\text{latt}} = \frac{1}{\Omega_0} \sum_{i=1}^{N_{\text{IR}}} p_i^{\text{d}} u_i, \quad (3)$$

where p_i^{d} is the polarity of the i -th IR mode, which can be obtained from the atomic Born effective charges and the mode eigenvector [8]. From these expressions, the equilibrium value of u_i for a given \mathcal{E} is calculated to be

$$u_i = \frac{p_i^{\text{d}}}{C_i} \mathcal{E}. \quad (4)$$

On the other hand, the assumption that our model crystal displays a linear ME effect implies

$$\Delta \mathcal{M}(\{u_i\}, \mathcal{E}) = \alpha_{\text{elec}} \mathcal{E} + \frac{1}{\Omega_0} \sum_{i=1}^{N_{\text{IR}}} p_i^{\text{m}} u_i, \quad (5)$$

where the u_i 's are again assumed to be independent of \mathcal{E} and we have introduced p_i^{m} parameters that quantify the magnetic response to the IR modes. Finally, by virtue of Eq. (4) we can write

$$\Delta \mathcal{M}(\mathcal{E}) = \alpha_{\text{elec}} \mathcal{E} + \frac{1}{\Omega_0} \sum_{i=1}^{N_{\text{IR}}} \frac{p_i^{\text{m}} p_i^{\text{d}}}{C_i} \mathcal{E}, \quad (6)$$

and it immediately follows that

$$\alpha_{\text{latt}} = \sum_{i=1}^{N_{\text{IR}}} \alpha_{\text{latt},i} = \frac{1}{\Omega_0} \sum_{i=1}^{N_{\text{IR}}} \frac{p_i^{\text{m}} p_i^{\text{d}}}{C_i}, \quad (7)$$

where mode-dependent contributions to α_{latt} have been defined. This equation encapsulates our method for an *ab initio* computation of the ME response. Its most remarkable feature is that all the parameters that appear in it can be computed without the need of simulating the material under applied electric or magnetic fields, which brings the calculation of ME effects within the scope of the most widely used DFT codes.

The above expression offers some insight into the microscopic ingredients needed to have a strong lattice-mediated ME response. In essence, one would like to have *soft* IR modes (i.e., with small C_i) that are highly polarizable (i.e., with large p_i^{d}) and cause a large magnetic response (i.e., with large p_i^{m}). Note that the p_i^{m} parameters can be viewed as the magnetic analogue of the polarities p_i^{d} associated to the dynamical charges. Also in analogy with p_i^{d} , p_i^{m} can be written as a sum of atomic contributions weighted by the corresponding components of the IR eigenvector. It is then clear that, in order to have IR modes with simultaneously large p_i^{d} and p_i^{m} , we need materials in which the magnetic atoms present large Born effective charges. While rare, this is the case of compounds like CaMnO_3 [3].

A few additional comments are in order. (1) The proposed approach can be used to simulate ME effects of arbitrary order in \mathcal{E} , but is restricted to couplings that are linear in the magnetic field. This limitation can be remedied by simulating the material under applied magnetic fields, which is relatively easy in comparison with treating finite electric fields in extended systems described with periodic boundary conditions [9]. (2) The ME response mediated by the strain (η) can be trivially included. More specifically, the above formulas are correct for paraelectrics, for which the leading strain terms in Eq. (2) are of the form η^2 and ηu_i^2 , and result in ME responses of order higher than linear. In ferroelectrics, on the other hand, there exist ηu_i terms that give a linear contribution to the response. (3) While the above derivation is made in terms of the eigenvectors of the force-constant matrix, one could imagine an analogous scheme using the IR eigenmodes of the dynamical matrix as structural variables. It would then be possible to model the dynamical ME response. (4) It is possible to derive the above results in a more general way, by working with an energy $E(\{u_i\}, \mathcal{E}; \{m_j\}, \mathcal{H})$ that includes the localized magnetic moments m_j and the magnetic field \mathcal{H} as independent variables of the system.

Results for Cr_2O_3 .— The work on magnetoelectrics starts with the prediction [10] and experimental confirmation [11, 12] that linear ME effects occur in Cr_2O_3 (chromia), which remains one of the simplest and best studied ME materials. Cr_2O_3 is an antiferromagnetic (AFM) insulator with a 10-atom unit cell and the magnetic structure sketched in Fig. 1. The magnetic easy axis lies along the rhombohedral direction c . The crystal has the magnetic space group $R\bar{3}'c'$, which preserves all the crystallographic symmetries of $R\bar{3}c$; thus, the compound is paraelectric. Cr_2O_3 presents six IR modes: two polarized along the rhombohedral c -axis, corresponding to the A_{2u} irreducible representation of $3m$, and four double-degenerate modes with E_u symmetry and polarization within the ab -plane. The linear ME tensor is diagonal with two independent terms: $\alpha_{aa} = \alpha_{bb} = \alpha_{\perp}$ and $\alpha_{cc} = \alpha_{\parallel}$. Naturally, the lattice-mediated part of α_{\perp} (α_{\parallel}) can be decomposed into contributions from the E_u (A_{2u}) modes, which we can compute with our method. (In the following we drop the “latt” subscript from the α 's to alleviate the notation.)

For the calculations we used the LDA [13] approximation to DFT as implemented in the plane-wave code VASP [15]. We used the PAW scheme [16] to represent the atomic cores. Only the nominal valence electrons were explicitly solved, which we checked is sufficient. Let us just note that all the *trivial* calculations involved in this study (e.g., for the equilibrium atomic structure, force-constant matrix, or induced polarizations [17]) were performed accurately and following well-established procedures, and that all of them were done at the collinear level. To obtain the p_i^{m} parameters in Eq. (7), we com-

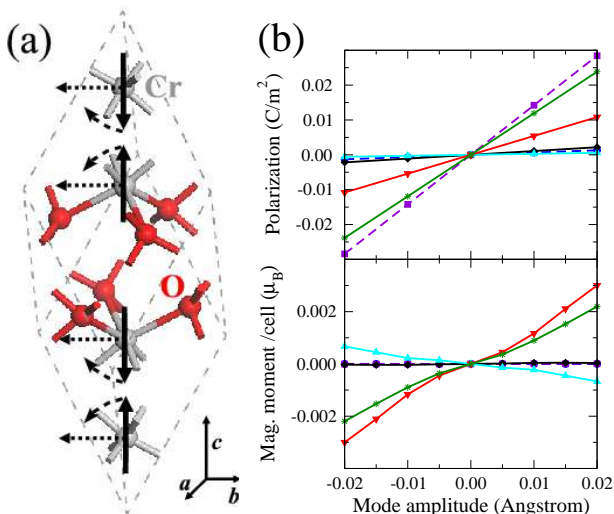


FIG. 1: Panel a: Primitive cell of Cr_2O_3 . Solid arrows represent the AFM ground state. Dashed arrows sketch the atomic displacements within the ab plane associated to a typical E_u IR mode, as well as the induced spin rotations that render a net magnetic moment. Panel b: Computed polarization and magnetization induced by the condensation of the IR modes. Dashed and solid lines correspond to A_{2u} and E_u modes, respectively. Note that the polarizations and magnetizations associated to the E_u (A_{2u}) modes lie within the ab plane (along the c direction). Note also that the magnetization induced by the A_{2u} modes is essentially zero.

puted the magnetic response upon condensation of the IR modes by running fully self-consistent non-collinear simulations including spin-orbit couplings. Interestingly, we found that a non-self-consistent approach, as usually employed for the computation of magnetic anisotropy energies, renders qualitatively incorrect results in this case. Let us also stress that, given the small magnitude of the energy differences associated to the ME effects in Cr_2O_3 , one has to be very careful with the choice of the parameters controlling the accuracy of the calculations. In particular, we found it necessary to use a very demanding stopping criterion for the self-consistent-field calculations (namely, energies converged down to 10^{-10} eV) to obtain, in a computationally robust way, reliable values of the magnetic moments induced by the condensation of the IR modes. We also determined that a k -point grid of at least $7 \times 7 \times 7$ is needed for accurate BZ integrations. (A magnetic easy axis in the ab -plane is incorrectly predicted if grids that are not dense enough are used.) The plane-wave cutoff was found to be less critical; we used 400 eV. We employed the “LDA+U” scheme of Dudarev *et al.* [18] for a better treatment of the $3d$ electrons of Cr. We chose $U_{\text{eff}} = 2$ eV, which renders results in acceptable agreement with experiment for the atomic structure, IR phonon frequencies, electronic band gap, and magnetic moments [19]. At any rate, we checked the choice of U_{eff} is not critical, even for the computation of ME coeffi-

TABLE I: Parameters of Eq. (7) computed for the IR modes of Cr_2O_3 . Modes are divided in two groups, A_{2u} and E_u , according to their symmetry. The last line shows the results for the two independent α coefficients, obtained from the addition of the corresponding mode contributions. The α ’s are given in Gaussian units (g.u.) [22].

	A_{2u} modes			E_u modes		
C_i (eV/ \AA^2)	10.8	25.7	10.4	16.9	21.6	32.5
p_i^d ($ e $)	0.39	8.52	0.65	0.16	3.24	7.14
p_i^m ($10^{-2} \mu_B/\text{\AA}$)	0.02	0.04	0.41	-2.70	11.32	8.51
α_i (10^{-4} g.u.)	0.00	0.00	0.01	-0.01	0.62	0.68
$\sum_i \alpha_i$ (10^{-4} g.u.)	$\alpha_{\parallel} = 0.00$			$\alpha_{\perp} = 1.30$		

cients. Finally, let us note the orbital degrees of freedom can be expected to be *quenched* in Cr_2O_3 ; thus, we neglected their contribution to the magnetization.

Table I and Fig. 1 summarize our results, which present the following features. (1) We obtain α_{\parallel} much smaller than α_{\perp} . Indeed, our calculations indicate that the magnetic response associated to the A_{2u} modes is nearly zero, and provide an explanation for such an effect. We find that, for the E_u modes, the induced in-plane magnetization occurs via a canting of the Cr spins, as sketched in Fig. 1. In contrast, in the case of the A_{2u} modes, no symmetry-allowed spin canting can induce a magnetization along the c direction. Instead, the simulations show that the magnetization originates from a tiny charge transfer between the spin-up and spin-down Cr sublattices. Probably, the smallness of the corresponding p_i^m coefficients reflects the relatively large energy cost associated to such a mechanism. (2) The ME response α_{\perp} is dominated by the hardest E_u modes and, interestingly, such a result could have been anticipated from the mode eigenvectors. More precisely, the two hardest modes present a relatively large Cr contribution, which should lead to relatively large values of p_i^m , as we indeed find. In addition, in the hardest eigenmode the Cr and O sublattices move rigidly and in opposite directions, which must result in a large p_i^d , exactly as found. (3) We obtain both positive (from three modes) and negative (from one mode) contributions to α_{\perp} . (Given the smallness of the magnetic effects computed, we have not tried to identify the electronic underpinnings of having positive or negative α_i ’s.) This result suggests that, in a general case, a small static ME effect may be the result of cancellations between contributions from different IR modes. Hence, large static ME effects will most likely be associated to compounds in which a single IR mode dominates the response.

To the best of our knowledge, the low temperature ME response of Cr_2O_3 is not totally understood, which reflects both the difficulties involved in ME measurements and the rich nature of the problem. The exper-

imental results at 4.2 K are quite scattered [23]: $|\alpha_{\perp}|$ ranges from 0.2×10^{-4} to 4.7×10^{-4} in Gaussian units (g.u.) and $|\alpha_{\parallel}|$ from 0.4×10^{-4} to 1.2×10^{-4} g.u. There are reasons to believe that the magnitude of the ME effects was underestimated in the early experiments [24], and that the largest coefficients measured [23, 25] are the most reliable ones. In particular, $|\alpha_{\perp}|$ probably lies somewhere between 2×10^{-4} and 4×10^{-4} g.u., which is remarkably close to our result. Interestingly, it is not clear how to explain this relatively large value of α_{\perp} in terms of the purely electronic mechanisms typically considered [25, 26, 27]. It is thus worth noting our computed lattice-mediated ME response is of the same magnitude as the one measured. As for the parallel response, all the experiments render $|\alpha_{\parallel}| < |\alpha_{\perp}|$ at low temperatures, but none reports an essentially zero value as we obtain. Our results are thus compatible with the notion that either a purely electronic mechanism, as the electric-field-induced g shift proposed in Ref. [27], or a magnetic effect not related to the ME coupling [26] is responsible for the non-zero α_{\parallel} at low temperatures.

In summary, we have introduced an efficient method to compute lattice-mediated magnetoelectric responses *ab initio*. We hope our work will enable a more effective interaction between theory and experiment in the search for materials that can be used in applications.

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[1] M. Fiebig, J. Phys. D: Appl. Phys. **38**, R123 (2005).
[2] W. Eerenstein, N.D. Mathur, and J.F. Scott, Nature **442**, 759 (2006).
[3] A. Filippetti and N.A. Hill, Phys. Rev. B **65**, 195120 (2002).
[4] C. Ederer and N.A. Spaldin, Curr. Opin. Solid State and Mater. Sci. **9**, 128 (2005).
[5] C.J. Fennie and K.M. Rabe, Phys. Rev. Lett. **97**, 267602 (2006).
[6] S. Picozzi, K. Yamauchi, B. Sanyal, I.A. Sergienko, and E. Dagotto, Phys. Rev. Lett. **99**, 227201 (2007).
[7] W.F. Brown, R.M. Hornreich, and S. Shtrikman, Phys. Rev. **168**, 574 (1968).
[8] Ph. Ghosez and J. Junquera, Ch. 134 of the *Handbook of Theoretical and Computational Nanotechnology*, M. Rieth and W. Schommers, Eds. (American Scientific Publisher, Stevenson Ranch, 2006).
[9] I. Souza, J. Íñiguez, and D. Vanderbilt, Phys. Rev. Lett. **89**, 117602 (2002).

[10] I.E. Dzyaloshinskii, J. Exp. Theo. Phys. (USSR) **37**, 881 (1959).
[11] D.N. Astrov, J. Exp. Theo. Phys. (USSR) **38**, 984 (1960); *ibid* **40**, 1035 (1961).
[12] V.J. Folen, G.T. Rado, and E.W. Stalder, Phys. Rev. Lett. **6**, 608 (1961); G.T. Rado and V.J. Folen, Phys. Rev. Lett. **7**, 310 (1961).
[13] J.P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981); D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980). The reason to perform LDA, instead of GGA, calculations is two-fold: the LDA is generally more accurate for ferroelectrics [14] and it results in a better convergence of VASP non-collinear calculations.
[14] K.M. Rabe and Ph. Ghosez in *Physics of Ferroelectrics: A Modern Perspective*, K. Rabe, Ch.H. Ahn, and J.-M. Triscone, Eds. (Springer-Verlag, Berlin Heidelberg, 2007).
[15] G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11169 (1996).
[16] P. E. Blochl, Phys. Rev. B **50**, 17953 (1994); G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[17] R.D. King-Smith and D. Vanderbilt, Phys. Rev. B **47**, 1651 (1993).
[18] S.L. Dudarev, G.A. Botton, S.Y. Savrasov, C.J. Humphreys, and A.P. Sutton, Phys. Rev. B **57**, 1505 (1998).
[19] We worked at the experimental volume (96 \AA^3); selected quantities were computed at the theoretical volume (92 \AA^3), and no significant difference was observed. Rhombohedral unit cell: $a = 5.37 \text{ \AA}$ and $\alpha = 54.66^\circ$; symmetry independent atoms: Cr at (x, x, x) with $x = 0.1536$ and O at $(0.9425, 0.5575, 1/4)$; band gap: $\sim 2.1 \text{ eV}$; magnetic moment per Cr: $\sim 2.8 \mu_B$. IR mode frequencies (cm^{-1}): A_{2u} (408, 597) and E_u (316, 455, 578, 653). These results are in reasonable agreement with experimental data and previous calculations reported in Refs. 20 and 21.
[20] G. Lucovsky, R.J. Sladek, and J.W. Allen, Phys. Rev. B **16**, 4716 (1977).
[21] A. Rohrbach, J. Hafner, and G. Kresse, Phys. Rev. B **70**, 125426 (2004).
[22] The conversion of units is described in J.-P. Rivera, Ferroelectrics **161**, 165 (1994). In short, the α 's we compute in SI units must be multiplied by $\mu_0 = 4\pi \times 10^{-7} \text{ Vs/(Am)}$, and then by $c = 3 \times 10^8 \text{ m/s}$, to obtain an adimensional quantity in Gaussian units.
[23] H. Wiegmann, A.G.M. Jansen, P. Wyder, J.-P. Rivera, and H. Schmid, Ferroelectrics **162**, 141 (1994).
[24] A major difficulty is related with the fact that different AFM domains may present ME effects of opposite sign [11, 12]. Hence, the magnitude of α measured in a sample in a multi-domain state will be smaller than that of the actual *intrinsic* response.
[25] E. Kita, K. Siratori, and A. Tasaki, J. Appl. Phys. **50**, 7748 (1979).
[26] G.T. Rado, Phys. Rev. Lett. **6**, 609 (1961); Phys. Rev. **128**, 2546 (1962).
[27] R. Hornreich and S. Shtrikman, Phys. Rev. **161**, 506 (1967).